Catalytic activity and selectivity of $Ru(=CHPh)Cl_2(PCy_3)_2$ in the metathesis of linear alkenes

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Abstract

Optimum conditions for the metathesis of internal linear alkenes, including fatty acid esters, in the presence of $Ru(=CHPh)Cl_2(PCy_3)_2$ as the catalyst, were found in dichloromethane and dichloroethane solutions at temperatures of 20–70°C. The reaction proceeded with high selectivity to primary metathesis products, which were formed as *trans/cis* mixtures. The final *trans/cis* ratios were close to the thermodynamic equilibrium values, regardless of the configuration of the substrate. The reaction rate of fatty acid esters was comparable to that of unsubstituted alkenes. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of well-defined single-component metal carbene complexes as homogeneous metathesis catalysts has opened up new prospects for the alkene metathesis reaction [1]. In particular, the ruthenium complexes of the type $Ru(=CHR)Cl_2(PR'_3)_2$ (R = $-CH=CPh_2$, Ph; R' = Ph, Cy, *i*-Pr) [2–5], which exhibit both high reactivity and high tolerance towards functional groups, have found a remarkable number of applications for a variety of metathesis reactions such as ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) [6–8]. The most active among them,

$Ru(=CHPh)Cl_2(PCy_3)_2$ (**1**), known as *Grubbs' catalyst*, is now commercially available.

Little attention has been paid so far to the catalyst $Ru(=CHR)Cl_2(PR'_3)_2$ in the metathesis of linear alkenes (Eq. (1), where R^1 and R^2 represent an alkyl group or hydrogen).

$$2\,R^1-CH=CH-R^2 \rightleftharpoons$$
$$R^1-CH=CH-R^1 + R^2-CH=CH-R^2 \qquad (1)$$
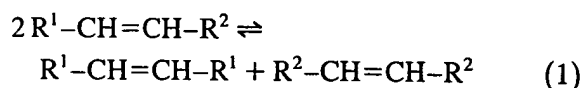
The few examples studied so far include two papers by Grubbs et al. [3,9] which focus on *cis*-2-pentene and terminal alkenes as substrates, respectively. [1]

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[1] During the preparation of this manuscript, a publication appeared describing a library of internal alkenes via metathesis using **1**. However, reaction rate and conversion data were not given [10].

In the case of linear internal alkenes, if the metathesis products remain in the reaction mixture, a statistical distribution of reactant and product molecules eventually results. This means that the reaction can reach only a 2:1:1 molar composition (i.e., 50% conversion). If a catalyst is also active for double-bond migration additional products can be formed by cross-metathesis reactions. This would result in a complex product mixture and in a decrease of the yield of the desired compounds.

In this paper, we explore possible applications of 1 for the metathesis of linear internal alkenes—with some emphasis on unsaturated fatty acid esters—in order to also observe possible activity of 1 for double-bond migration. The trans/cis composition of the alkenes has also been followed with the progress of metathesis using 1.

2. Experimental

All manipulations were performed using standard Schlenk tube techniques under an atmosphere of nitrogen, which was purified by passage through columns of Cu/Al_2O_3 (BASF R3-11) and KOH. NMR spectra were measured with a Bruker AMX-300 spectrometer. The field desorption mass spectrum (FDMS) of 1 was measured with a JEOL JMS SX/SX102A mass spectrometer.

2.1. Materials

Hexane and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane, 1,2-dichloroethane and 1,2-dichlorobenzene were passed through columns of activated alumina and refluxed with CaH_2 for three days. trans/cis-4-Nonene, methyl oleate (methyl cis-9-octadecenoate), methyl elaidate (methyl trans-9-octadecenoate) and trans-4-decene were purchased from Fluka; trans-3-heptene, cis-3-heptene and trans-5-decene were purchased from Aldrich; methyl erucate (methyl cis-13-docosenoate) was purchased from Sigma. The

alkenes were purified by passing through activated alumina and distillation. 1 was prepared from $RuCl_2(PPh_3)_3$ according to Ref. [5]. ^1H and ^{31}P NMR spectra were in agreement with the published data. FDMS of 1: m/z (rel. intensity) = 823 (M^+ with isotopic pattern of Ru, 100%), 296 (PCy_3O, 25%), 280 (PCy_3, 40%). $RuCl_2(PPh_3)_3$ was prepared from $RuCl_3$ hydrate [11].

2.2. Metathesis experiments

In a typical experiment, 3.3 mg (4.01×10^{-3} mmol) of $Ru(=CHPh)Cl_2(PCy_3)_2$ was used to which 1.30 ml of the appropriate solvent was added, followed by a mixture (0.60 ml) of 2.21 mmol of an alkene and an internal standard. The resulting solution was vigorously stirred. Nonane or nonadecane (in the case of fatty acid esters) were used as internal standards. The progress of metathesis was monitored by sampling through a septum at suitable intervals. The catalyst in these samples was immediately quenched with an excess of ethyl vinyl ether [5]. The samples were analysed by GC; the reaction products were identified by GC/MS.

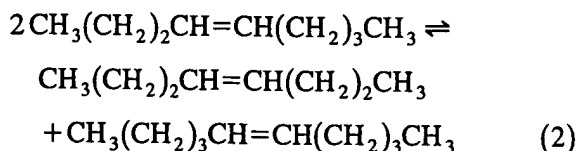### 2.3. NMR measurements of $Ru(=CHPh)Cl_2$-$(PCy_3)_2$ in a sealed tube

Commercial purity CD_2Cl_2, sealed and stored under nitrogen, was used. $Ru(=CHPh)Cl_2$-$(PCy_3)_2$ (6.1 mg, 7.41×10^{-3} mmol) was placed in a NMR tube under nitrogen. 0.60 ml of CD_2Cl_2 was added and the tube was flame-sealed. ^1H and ^{31}P NMR spectra were measured after two hours, 3, 7 and 21 days. The tube was kept at room temperature (ca. 20°C) during that time.

3. Results and discussion

3.1. Effect of solvent

In order to find the most suitable conditions for the metathesis with the ruthenium catalyst,

we first examined the effect of the solvent. As a model reaction we chose the metathesis of 4-nonene (Eq. (2)).

$$2 CH_3(CH_2)_2CH=CH(CH_2)_3CH_3 \rightleftharpoons$$

$$CH_3(CH_2)_2CH=CH(CH_2)_2CH_3$$

$$+ CH_3(CH_2)_3CH=CH(CH_2)_3CH_3 \qquad (2)$$

Large differences in activities of 1 were found in the selected solvents (Table 1). The best performance was observed in dichloromethane (DCM) and 1,2-dichloroethane (DCE). The run in hexane was the slowest and did not reach equilibrium at all (29% conversion after 47 h), while an attempt in neat alkene was ineffective due to limited catalyst solubility.
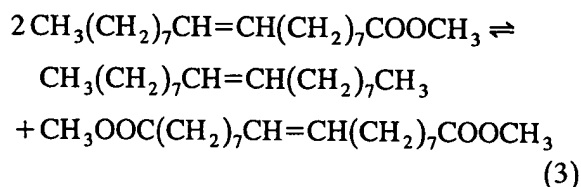
3.2. Effect of temperature

An experiment at elevated temperature (Table 1, entry 6) showed that the catalyst performance could be significantly improved by using a higher temperature. Therefore, the influence of the temperature on the activity of 1 was further investigated at temperatures up to 70°C with 4-nonene as the substrate (Fig. 1). The two

solvents DCM and DCE gave essentially the same reaction rates as illustrated by runs at 20°C and 40°C. Further improvement was achieved at 70°C in DCE.

3.3. Activity and selectivity

Table 2 shows the results of the metathesis of various normal and functionalized internal olefins such as methyl oleate (Eq. (3)).

$$2 CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3 \rightleftharpoons$$

$$CH_3(CH_2)_7CH=CH(CH_2)_7CH_3$$

$$+ CH_3OOC(CH_2)_7CH=CH(CH_2)_7COOCH_3 \qquad (3)$$

The data after 4 h of reaction are shown with the exception of runs that approached equilibrium within a shorter time. Comparing entries 4 and 9 as well as 6 and 8 shows that the activity of 1 is not significantly decreased by the presence of an ester group. Slightly lower rates for the metathesis of fatty acid esters may also be due to the larger size of these substrates, a suggestion supported by observations of Grubbs and coworkers [9,12] that steric factors are im-

Table 1
Activity of $Ru(=CHPh)Cl_2(PCy_3)_2$ (1) for the metathesis of *trans/cis*-4-nonene[a] in selected solvents

Entry	Solvent	Concentration of 1 (mM)	Temperature (°C)	TOF[b] (equiv./h)	Time (h)	Conversion[c] (%)
1	Hexane	2.06	20	1.7	4	5.8
2	Diethyl ether	2.61	20	4.5	4	17
3	Dichloromethane	5.85	20	22	4	45
4	1,2-Dichlorobenzene	6.01	20	9.0	4	35
5	1,2-Dichloroethane	6.07	20	30	3.5	50
6	1,2-Dichloroethane	6.07	50	130	0.5	49
7	1,2-Dichloroethane[d]	6.07	20	47	4	28
8	Neat	–[e]	20	7.1	4	26

Reaction conditions: molar ratio 4-nonene:1 = 100:1; for entries 1 and 2 the lower concentrations are a consequence of the limited solubility of the catalyst.
[a] *Trans/cis* ratio 0.86.
[b] Turnover frequency calculated according to Ref. [3] as the point at which conversion to $C_8 + C_{10}$ reached 40% by extrapolating the first part of reaction were the rate of metathesis is approximately pseudo-first order.
[c] Conversion to $C_8 + C_{10}$ calculated as $([C_8] + [C_{10}])/([C_8] + [C_9] + [C_{10}])$.
[d] 6.10 equiv. of CuCl added to the solution of 1 before the substrate.
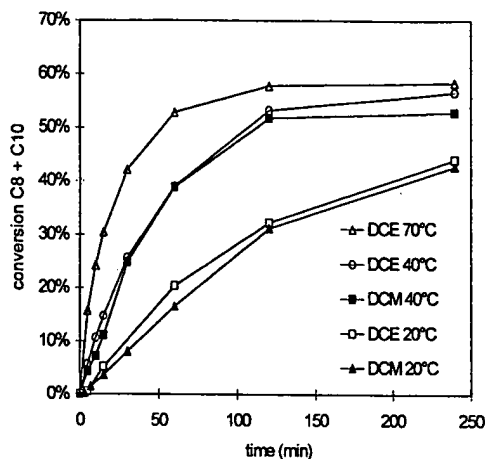[e] Catalyst not completely dissolved.

Fig. 1. Effect of the temperature on the metathesis of *trans / cis*-4-nonene with Ru(=CHPh)Cl₂(PCy₃)₂ (1); DCM = dichloromethane, DCE = 1,2-dichloroethane. Reaction conditions: ratio *trans / cis*-4-nonene:1 = 550:1; concentration of 1 = 3 mM.

verse steric interaction with the bulky phosphine, which results in a lower rate of initial alkene binding. Reaction in neat alkene (Table 2, entry 12) is again unfavourable. The catalyst did not completely dissolve in this amount of alkene and a homogeneous solution was obtained only after one hour, with the conversion reaching 45% after 4 days.

The selectivities in entries 1, 2 and 3 show that an increase in the temperature up to 70°C does not affect the selectivity of 1. The selectivity significantly dropped in refluxing DCE (83°C) as illustrated by a run with methyl elaidate (Table 2, entry 10). In the other cases the selectivity was somewhat less than 100%, which just reflects the purity of the substrates.

In order to further demonstrate the selectivity of 1 we chose a symmetrical alkene, viz. *trans*-5-decene (Eq. (1), $R^1 = R^2 = CH_3(CH_2)_3-$). Any conversion with this substrate, apart from *trans–cis* isomerization, would mean that the catalyst is also active for double bond shift. The metathesis activity of the catalyst in this case was followed as *trans/cis* isomerization of the substrate. Indeed, almost no conversion (< 1%)

portant in the reactivity of 1. Comparing entries 6 and 7 as well as 8 and 9 in Table 2 indicates that *cis*-alkenes react faster with 1 than *trans*-alkenes. This is explained by an easier binding of a *cis*-alkene to the Ru metal than of a *trans*-alkene. In the latter case there is an ad-

Table 2
Activity and selectivity of Ru(=CHPh)Cl₂(PCy₃)₂ (1) for the metathesis of selected substrates

Entry	Substrate	Temperature (°C)	Time (h)	Conversion of substrate (%)	Selectivity[a] (%)
1	*trans/cis*-4-Nonene[b]	20	4	56	89
2	*trans/cis*-4-Nonene[b]	40	1	50	89
3	*trans/cis*-4-Nonene[b]	70	0.5	54	90
4	*trans*-4-Decene	20	4	36	96
5	*trans*-5-Decene	20	4	< 1	–
6	*cis*-3-Heptene	20	4	50	83
7	*trans*-3-Heptene	20	4	32	90
8	Methyl oleate[c]	20	4	40	96
9	Methyl elaidate[d]	20	4	36	88
10	Methyl elaidate	83	1	54	65
11	Methyl erucate[e]	20	4	39	87
12	*trans*-4-Decene *neat*	20	4	10	–

Reaction conditions: 3 mM solutions in DCE or DCM except entry 12 (no solvent), molar ratio substrate:1 = 550:1.
[a] Selectivity to self-metathesis products of the substrate.
[b] *Trans/cis* ratio 0.86.
[c] Methyl *cis*-9-octadecenoate.
[d] Methyl *trans*-9-octadecenoate.
[e] Methyl *cis*-13-docosenoate.

to any other new product was observed (Table 2, entry 5).

3.4. Stability

The loss of **1** becomes a significant problem at extended reaction times. We clearly observed a slow decomposition of the catalyst in all runs, which was visualised as a change in colour of the reaction mixture from red to greenish-brown; no precipitate was seen in any of our experiments. To draw further conclusions on the stability of **1** we measured its ^{1}H NMR (Fig. 2) and ^{31}P NMR spectra in a sealed tube in a CD_2Cl_2 solution. We estimate the oxygen concentration in the purified nitrogen at 1 ppm, which means that a small and constant amount of oxygen was present in this system. Decomposition of **1** is evident as the intensity of the carbene proton peak at 20.0 ppm slowly declines. Formation of other carbenes from **1** is
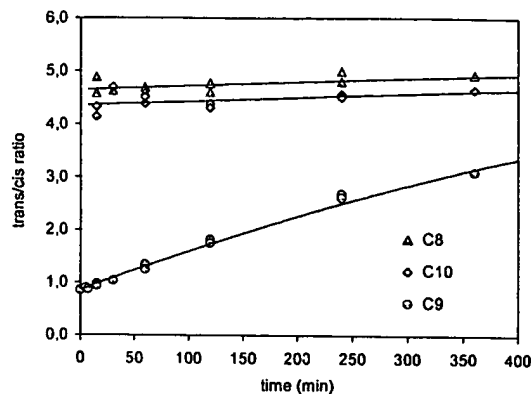

Fig. 3. *Trans / cis* ratios of products and substrate in the metathesis of *trans/cis*-4-nonene with Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$ (**1**) at room temperature; C8 = 4-octene, C9 = 4-nonene, C10 = 5-decene. Reaction conditions: ratio *trans/cis*-4-nonene:**1** = 550:1; concentration of **1** = 3 mM.

excluded since new resonances in the range of 22–19 ppm are not observed. Similarly, in the ^{31}P NMR spectra, apart from a peak of **1** at 36.7 ppm, new resonances appeared at 49.7, 35.7 and
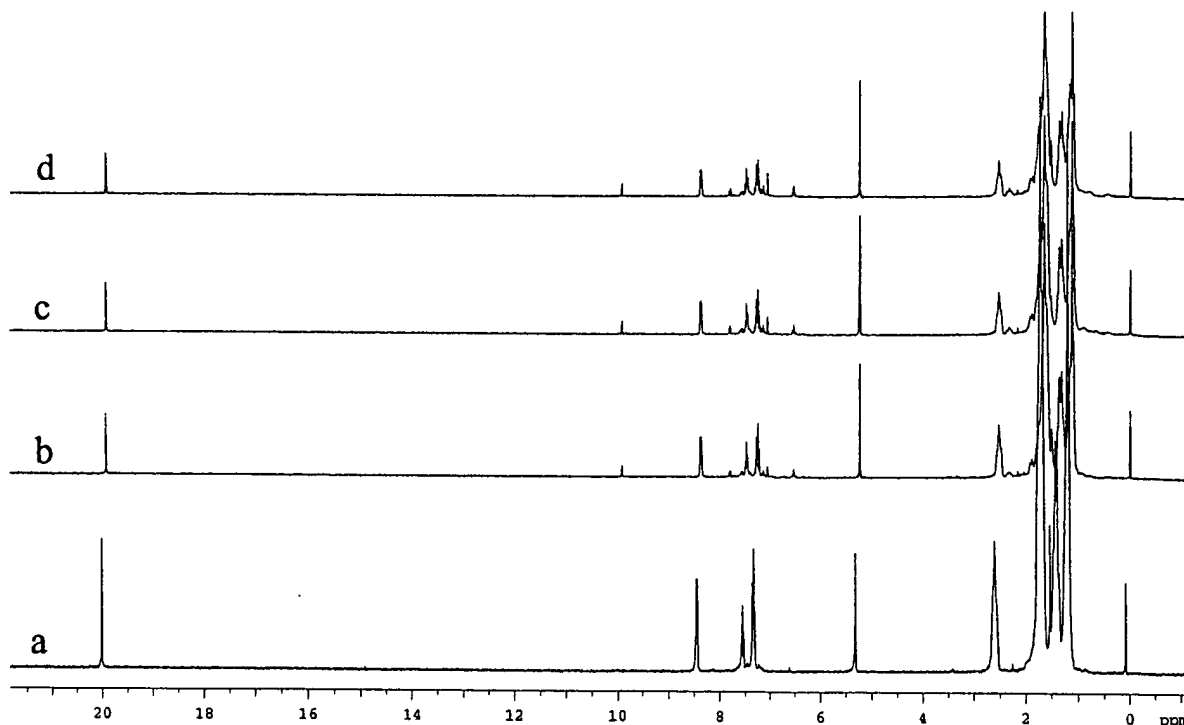

Fig. 2. ^{1}H NMR spectra of Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$ in CD_2Cl_2 recorded after (a) 2 h; (b) 3 days; (c) 7 days; (d) 21 days.

25.0 ppm; free tricyclohexylphosphine is however not detected with this technique. Approximately 60% of the starting amount of 1 decomposed in this experiment: the solution turned red-brown but no precipitate was seen. A solution of 1 in dichloromethane exposed to air decomposed overnight to a brown solution.

From these observations, it is clear that the metathesis activity of 1 slowly declines at extended reaction times. Therefore, we also measured the limits of 1. The maximum turnover number (TON) of 2500 was achieved with methyl oleate after 48 h when 5500 equivalents of this substrate were reacted at 20°C. The turnover number was somewhat lower (1900) for trans-4-decene under the same conditions; increase in the temperature to 65°C resulted in higher initial reaction rates but the metathesis stopped at 27% conversion after 2 h.

3.5. Stereochemistry

Fig. 3 shows a typical example of the trans/cis product ratios in the metathesis of trans/cis-4-nonene. As soon as the reaction
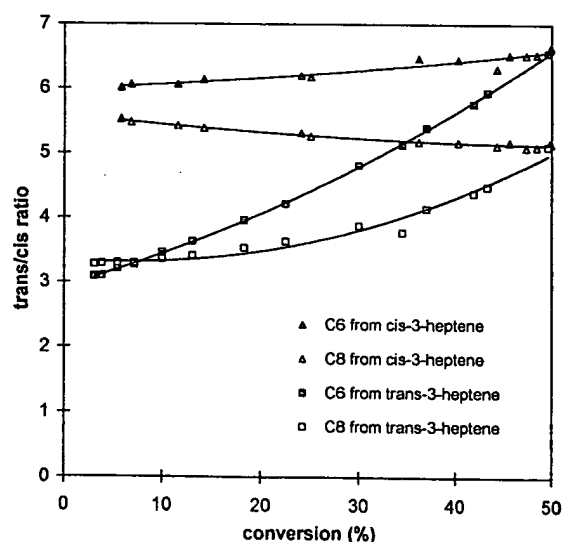

Fig. 4. Stereochemistry of 3-hexene (C6) and 4-octene (C8) formed in the metathesis of cis-3-heptene and trans-3-heptene with Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$ (1). Runs in DCM at 20°C with ratio substrate:1 = 550:1; concentration of 1 = 3 mM.

products could be properly measured, we observed trans/cis ratios of 4-octene and 5-decene close to their equilibrium values, [2] while the substrate (starting trans/cis ratio 0.86) slowly isomerized to its equilibrium composition. The same stereochemical progress in metathesis using 1 was found for all substrates listed in Table 2.

Moderate stereoselectivity is noticed when experiments with trans- and cis-3-heptene are compared. cis-3-Heptene yielded products with higher trans content than trans-3-heptene (Fig. 4). This trend is clearly seen at low conversion; at high conversion the mixtures approach the same thermodynamic composition.

4. Conclusions

Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$ (1) has been shown to selectively catalyze the metathesis of internal alkenes and to have no activity for alkene isomerization. The catalyst can be used at temperatures up to 70°C without any loss in selectivity.

Slow decomposition of 1 is clearly observed in all runs despite the use of the protective atmosphere of purified nitrogen. Decrease in metathesis activity is inevitable since new carbene species are not formed from 1. Therefore, certain limits of the applicability of 1 are apparent from this contribution. Under the experimental conditions described in this paper the maximum TON for the metathesis of methyl oleate is 2500.

Acknowledgements

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[2] Ref. [1], p. 117.

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